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(54) Title: ELECTRICALLY CONDUCTING PLASTICIZER COMPOSITION AND PROCESS FOR THE PRODUCTION THEREOF

(57) Abstract: The invention relates to an electrically conductive plasticizer composition and to a process for the preparation thereof. The composition according to the invention comprises 50-95 parts by weight of a plasticizer for thermoplastics and 50-5 parts by weight of polyaniline and its counter-ion, which together form a doped polyaniline complex dissolved or dispersed in the plasticizer. By means of the invention it is possible to prepare, for example, an electrically conductive PVC film by mixing together 10-50 parts by weight of the plasticizer composition, 1-90 parts by weight of a PVC emulsion and 0-10 parts by weight of auxiliary agents and colorants, known *per se*, to form a PVC mixture, by spreading the mixture onto a substrate to form a continuous layer, and by solidifying the composition to form an electrically conductive film.



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Electrically conducting plasticizer composition and process for the production thereof

The present invention relates to a plasticizer composition according to the preamble of Claim 1.

- 5 The electrical conductivity of such a composition is in general approx. $10^{-2} \dots 10^{-9}$ S/cm.

The invention also relates to a process according to the preamble of Claim 9 for preparing an electrically conductive plasticizer composition and to a process according to Claim 18 for preparing an electrically conductive PVC film.

- 10 A fabric coated with polyvinyl chloride (PVC) can be used for manufacturing, for example, hoses. These are used in tunnels and mines as air-conditioning pipes. Fabric hoses are practical for this purpose, because they are easy to install in place and the support structures required by them are simple. However, particularly in the dusty conditions of a mine there tends to form in a plastic hose static electricity, which may cause sparking. This may, of course, be very dangerous. For this reason the hoses should be made electrically
15 conductive so that static electricity cannot be formed.

- It is known to manufacture electrically conductive hoses by using carbon powder as a conductive component in the PVC coating. The coating is carried out by a melt-processing technique such as calendering. One example of the state of the art is US patent publication 5,066,422, disclosing carbon-black-containing PVC mixtures from which films can be
20 processed.

- There are considerable disadvantages associated with the prior known technology. Thus, carbon powder tends to dust and is therefore highly soiling. The dyeing of the product is also difficult, since the carbon dust gives the product a black basic color. Furthermore, it is difficult by means of carbon dust to regulate with precision the conductive properties of a
25 fabric without worsening its mechanical properties.

The object of the present invention is to eliminate the disadvantages associated with prior known technology and to provide a clean production technology for manufacturing

electrically conductive films. It is a particular object of the invention to provide an electrically conductive plasticizer composition by means of which it is possible to modify the conductivity of a polymer composition. It is also an object of the invention to provide a composition from which it is possible to manufacture an easily dyed film having very high conductivity values and high mechanical strength.

The invention is based on the idea that an electrically conductive plasticizer composition having a conductivity of $10^{-2} \dots 10^{-9}$ S/cm is prepared by mixing a plasticizer with polyaniline in a non-conductive form in order to form a plasticizer mixture and by adding to the plasticizer mixture a counter-ion for the non-conductive polyaniline to dope the polyaniline and to form a doped plasticizer composition. Such a plasticizer composition typically comprises approx. 50 – 95 parts by weight of a plasticizer for thermoplastics and 50 – 5 parts by weight of the polyaniline and its counter-ion, which together form a doped polyaniline complex dissolved or dispersed in the plasticizer.

From the plasticizer composition it is possible to manufacture a conductive PVC film by spreading onto a substrate a fluid PVC mixture containing this composition to form a layer, whereafter the mixture is allowed to solidify so that a film is formed. The film may, when necessary, be detached from the substrate (e.g. transfer paper).

More precisely, the plasticizer composition according to the invention is mainly characterized in what is stated in the characterizing part of Claim 1.

The process according to the invention for producing a plasticizer composition is for its part characterized in what is stated in the characterizing part of Claim 9, and the process according to the invention for manufacturing an electrically conductive PVC film is characterized in what is stated in the characterizing part of Claim 18.

Considerable advantages are gained through the invention. Thus, the invention can be used advantageously for producing an electrically conductive plasticizer composition that can be mixed with many different polymers, in particular thermoplastics, whereby a migration-free polymer blend is obtained. It can be used for manufacturing films, sheets and other similar polymer products which can be joined by, for example, welding. The polyaniline is dissolved or dispersed in the plasticizer, in which case the processing of the composition

and its mixing with polymer dispersions is easy. The electrical conductivity can be regulated by means of the amounts of the polyaniline and its dopant. The conductive component does not have a significant effect on the strength properties of the polymer product.

- 5 A solvent of polyaniline is not used in the present invention. Thereby the advantage is gained that the compositions can be formulated freely when a PANI solvent setting its limitations on the plasticizers is not used. However, preferably monomeric plasticizers are used in the invention.

- 10 In the invention, first an electrically conductive plasticizer composition is prepared which does not contain a thermoplastic. In this case the use of the plasticizer composition is not limited by a thermoplastic polymer already present in it.

Doping is carried out as part of the process for preparing the plasticizer composition when the starting point is the emeraldine base of polyaniline. When doping is carried out as a part of the preparation of the plasticizer composition, the doping can be regulated.

- 15 The obtained plasticizer composition is acidic, i.e. the polyaniline is in a conductive form. The plasticization process is preferably such (cf. Example 6 below) that the composition produced by it can be used for the manufacture of a PVC film without separate roll-mill grinding and, nevertheless, a well conductive final product is obtained.

- 20 The invention will be examined below with the help of a detailed description and several embodiment examples.

- As was noted above, the plasticizer composition according to the invention is electrically conductive. Its conductivity is in this case usually within the range $10^{-2} \dots 10^{-9}$ S/cm, typically higher than approx. 10^{-6} S/cm. The composition contains at least two components, namely a plasticizer for thermoplastics and a doped polyaniline complex. The latter is dissolved or dispersed in the plasticizer so that the solid particles will not separate from the composition during standing. Typically the particle size of the polyaniline complex in the plasticizer phase is smaller than 100 μm , usually smaller than 50 μm , preferably approx. 1 - 30 μm .
- 25

The proportion of plasticizer of the weight of the plasticizer composition is in general over one-half, although the concentration limits may vary widely. Most preferably the composition contains 50 – 99 parts by weight of a plasticizer and 1 – 50 parts by weight of a doped polyaniline complex. However, the composition may also contain other components, of which the most important are a dopant not bonded to the polyaniline complex and any possible additives and auxiliaries, such as metal compounds used for adjusting the pH value.

The plasticiser for thermoplastics is usually selected from the group including dialkyl phthalates; dialkyl terephthalates; trialkyl and triaryl phosphates; aliphatic acid esters, such as dialkyl adipate and dialkyl sebacate; sulfonic and benzene acid esters; epoxidized oils; and mixtures thereof. These are typical plasticizers used as plasticizers for PVC. Dialkyl phthalates the alkyl groups of which are similar or different and which comprise a linear or branched carbon chain of 1 – 9 carbon atoms are considered preferred plasticizers. Especially preferred are in this case C₇...C₉ dialkyl phthalates, i.e. mixtures of such esters, as well as dioctyl phthalate and di-iso-octyl phthalate.

In an aniline polymer the monomer is aniline or its derivative, the nitrogen atom of which is as a rule bonded to the carbon in the para position of the benzene ring of the subsequent unit. Unsubstituted polyaniline may appear in various forms, of which the so-called emeraldine form is in general used for conductive polymer applications. Polyaniline can be doped so as to become a conductive polyaniline complex in particular with protonic acids, of which some examples are HCl, H₂SO₄, HNO₃, HClO₄, HBF₄, HPF₆, HF, phosphoric acids, sulfonic acids, picric acid, n-nitrobenzene acid, dichloroacetic acid, and polymeric acids. Preferably a functional acid is used for the doping, for example sulfonic acid, in particular an aromatic sulfonic acid such as dodecylbenzenesulfonic acid (DBSA), camphor sulfonic acid, para-toluenesulfonic or phenolsulfonic acid. Acid can be used in excess for plasticizing the mixture. In this case a suitable metal compound, such as zinc oxide, can be used for compensating for the acidity. It is also possible to add a calcium compound, such as calcium carbonate. The pH of the mixture is, for example, 3 – 8, usually approx. 4 – 7. The preparing of polyaniline complexes is described in detail in, for example, published EP Applications Nos. 545 729 and 582 919 and FI Patent Applications Nos. 932557, 932578 and 940626.

The polyaniline complex preferably contains a polyaniline, such as a polyaniline of the emeraldine form, 1 – 20 % by weight, preferably 4 – 10 % by weight, and a doping acid, such as DBSA, 50 – 90 % by weight, preferably 60 – 85 % by weight.

5 An example of a preferred plasticizer composition is a composition that comprises polyaniline approx. 3 – 8 parts by weight, plasticizer approx. 70 – 90 parts by weight, and a counter-ion for the polyaniline approx. 5 – 20 parts by weight, the amount of counter-ion being in parts by weight approx. 2- to 4-fold the amount of polyaniline. In addition it contains an inorganic compound approx. 1 – 10 %, calculated from the amount of the dopant, the compound at least partly neutralizing the excess of dopant and thereby raising
10 the pH value of the composition to a suitable level. When mixed with a PVC emulsion, the composition forms a substantially non-migrating PVC blend.

According to the invention, the composition described above can be prepared in a two-step process. In the first step, the plasticizer is mixed with a polyaniline in a non-conductive form in order to form a plasticizer mixture. The ingredients of the plasticizer composition
15 are usually mixed together substantially without additional heating. However, the temperature of the composition rises during the mixing and varies during the mixing operation between 25 and 50 °C.

In the second step, to the plasticizer mixture thus produced a counter-ion for the non-conductive polyaniline is added in order to dope the polyaniline and to form a doped
20 plasticizer composition. The doped plasticizer composition is mixed for 1 – 48 hours at approx. 30 – 50 °C. However, the temperature may also be higher. In this case to the plasticizer mixture a doping mixture is added which comprises a counter-ion for the polyaniline and an activator capable of accelerating the doping. The activator is preferably a volatile compound that can be removed from the plasticizer composition by vaporization.
25 Such activators include alkanic acids, in particular formic acid and acetic acid, formic acid being especially advantageous. Preferably the activator is removed by means of vacuum and by raising the temperature of the composition to approx. 35 – 150 °C.

According to a preferred embodiment, 3 – 8 parts by weight of a polyaniline and approx. 70 – 90 parts by weight of a plasticizer are mixed to form a plasticizer mixture, and to this

mixture is added a dopant mixture that contains approx. 5 – 20 parts by weight of a counter-ion for the polyaniline and 1 – 10 parts by weight of activator.

The plasticizer composition described above can be used for manufacturing desired electrically conductive polymer films by surfacing or coating a suitable substrate with a mixture of the plasticizer composition and a polymer dispersion. The coating can be carried out by the spread-coating blade technique or the roller coating technique.

By "spread coating technique" is meant here generally coating methods in which a fluid polyaniline complex mixture is first spread onto a backing or a corresponding substrate by means of spread coating blades or rollers, whereafter the mixture is cured or solidified to form a film. The application mixtures most preferably contain a fluidizer, for example a plasticizer or solvent by means of which the desired fluidity is obtained for the mixture. The mixture can in general be cured (i.e. hardened) by heating. In the heating, volatiles, such as solvent, are also removed.

In general some other plastic and additives are also added to the mixture. The coating is preferably carried out by the spread-coating blade technique, wherein the plastic blend is spread onto a web of fabric into a uniform layer by means of a spread-coating blade. After the spread coating, the web is preferably directed to a curing kiln, where the mixture forms a continuous film on the fabric. After the curing, any post-treatment possibly needed, such as smoothing or patterning and cooling, is carried out.

The obtained surface resistance of the product varies according to the amount of polyaniline complex and the thickness of the coating. The surface resistance is, for example, approx. $10^4 - 10^9$, preferably $10^5 - 10^8 \Omega/\text{sq}$.

A strong and flexible fabric can be manufactured by the process according to the invention. A lacquer-like coating can be produced on the fabric. The fabric can be used for manufacturing a hose by joining the edges of the web together. The joining can be carried out by high-frequency welding. The hose can be used in particular as ventilation tube for mines and tunnels.

The fabric can also be used in other applications requiring protection against static electricity or electromagnetic radiation. The uses may include, for example, protective covers, storage containers (e.g. biogas collection bags) and conveyor belts, used in industry in situations in which there is a fire or explosion hazard. Potential uses also include
5 protection for electronic equipment or military hardware. The fabric is best applicable to uses where it is not greatly exposed to UV radiation.

For producing a spread-coating mixture, such as a paste, a solid polyaniline complex can be mixed with a suitable fluidizer, such as a plasticizer or a solvent. In order to obtain good mixing, it is advisable first to grind the polyaniline complex by means of, for example, a
10 pin mill to a particle size as small as possible. A suitable particle size is, for example, 1 – 200 μm , in particular 5 - 100 μm , preferably 10 – 50 μm .

In addition to a polyaniline complex, there is used in the mixture preferably another compatible plastic, in particular PVC. Other usable plastics include polyacrylates, polyurethanes, polyethylene vinyl acetate, polyvinylidene chloride, polyvinyl acetate,
15 polyvinyl alcohol, synthetic latexes, silicones, epoxy resins, and suitable blends thereof (e.g. ethylvinyl acetate and PVC).

PVC is preferably of an emulsion type having a particle size below 60 μm . The mixture may contain sulfonamide as an antistatic additive.

The proportion of the polyaniline complex in the plastic blend of the final coating may be,
20 for example, 0.1 – 30 % by weight, preferably 1 – 20 % by weight, most preferably 5 – 15 % by weight.

Furthermore, suitable additives such as plasticizers, stabilizers, fire retardants, colorants, slip agents, and modifiers can be used in the mixture. The plasticizers most commonly used in PVC products are dialkyl phthalates, dialkyl terephthalates, trialkyl or triaryl
25 phosphates, aliphatic acid esters such as dialkyl diapate and dialkyl sebasate, sulfonic or benzene acid esters, epoxidized oils, and mixtures thereof. The stabilizers most commonly used are metal soaps, inorganic salts (e.g. barium salts and lead salts), organo-tin compounds, and epoxy compounds. Both organic and inorganic suitable agents can be used

as colorants. The slip agents may be, for example, long-chain alcohols or various waxy substances.

The application substrate used may be, for example, fabric, paper, cardboard or similar film-like and/or sheet-like substrates. Various woven and non-woven fabrics can be mentioned as backings. The woven material may be, for example, polyester or polyamide. The backing is usually coated on both sides with, for example, PVC or a halogen-free plastic, such as a blend of polyethylene methacrylic acid and polyethylene. An additive enhancing the adhesion of the coating may be added to the backing.

A suitable backing is obtained, for example, by coating a net fabric with a PVC blend first by spread coating and then by calendering. If the thread count of the fabric is greater than approx. 6.5 threads/cm, mere spread coating will suffice.

When another plastic is used in the coating blend in addition to the polyaniline complex, it is possible first to make a dry blend of the plastics, and the desired fluidizer and possible additives are added to the blend thereafter. The preparation of dry blends is described in, for example, published EP applications Nos. 497 514 and FI Patent Applications Nos. 935889 and 941783. Alternatively it is possible to add to the polyaniline complex a fluidizer, a plastic, and any desired additives.

The following non-limiting examples illustrate the invention:

Example 1

Effect of the type of dodecylbenzenesulfonic acid on the properties of the end product

Example 1A Ufacid TPB as the dodecylbenzenesulfonic acid

4.68 g of polyaniline (Panipol Oy, EBR1 Lot 28) and 80.2 g of dioctylphthalate plasticizer (Bisoflex DOP) were mixed using a magnetic stirrer in a reactor for 5 min. A doping acid mixture prepared by mixing 15.12 g of dodecylbenzenesulfonic acid (Ufacid TPB, Unger Fabrikker A/S) and 6.5 g of an 85 % formic acid at room temperature for 5 min was added to the mixture. The acids were added in the course of approx. 10 min. During the adding, the temperature of the reaction mixture rose from room temperature to approx. 35 °C, at

which temperature the reaction was continued for a total of 24 h by stirring the mixture with a magnetic stirrer throughout the reaction. On the following day, the formic acid was evaporated out from the product in the course of approx. 8 h. At the same time the temperature of the product was gradually raised to 55 °C. After the distillation of the formic acid ended, the product was cooled. A conductive PVC film was made on a laboratory scale according to the following formula:

- 50 g of the above-mentioned conductive polyaniline complex
- 50 g of emulsion PVC
- 2 g of stabilizer
- 10 ▪ 3 g of carbon-black paste or titanium oxide TiO_2 (colorant)

The materials were mixed together carefully. After the mixing, the mixture was comminuted further in a paste mill. The paste-mill treatment rendered the mixture more homogeneous and minimized its granularity.

Thereafter 20 g of isopropanol was added to the comminuted mixture under careful mixing. After the mixing, a woven textile fabric was coated on both sides by the spread coating method. The PVC film formed in connection with the coating was kiln-treated at 165 °C for 2.5 minutes, whereby it gelled to form a completed product.

In the tests carried out, the surface resistance was $1.2 + E5 \Omega/\text{sq}$.

Example 1B Ufacid K as the dodecylbenzenesulfonic acid

20 An experiment according to Example 1A was carried out by merely replacing the dodecylbenzenesulfonic acid type Ufacid TPB with Ufacid K. The conductive complex had a lower viscosity and was easier to process in the tests than the complex of Example 1A. The surface resistance of the end product was $1.0 \dots 1.2 + E5 \Omega/\text{sq}$.

Example 1C Ufacid KW as the dodecylbenzenesulfonic acid

25 An experiment according to Example 1A was carried out by merely replacing the dodecylbenzenesulfonic acid type Ufacid TPB with Ufacid KW. The conductive complex

had a lower viscosity and was easier to process than the complex of Example 1A. In the tests the surface resistance of the end product was higher than in Examples 1A and 1B, being approx. $1.5 \times 10^6 \Omega/\text{sq}$.

Example 2

5 Effect of the reaction time on the quality of the final product

1.81 kg of polyaniline (Panipol Oy, EBR1 Lot 28) and 28.96 kg of dioctylphthalate plasticizer (Bisoflex DOP) were mixed in a reactor for 15 min. A doping acid mixture prepared by mixing 5.46 kg of dodecylbenzenesulfonic acid (Ufacid K) and 2.35 kg of an 85 % formic acid for 15 min at room temperature was added to the mixture. The acids were
10 added in the course of approx. 20 min. During the adding, the temperature of the reaction mixture rose from room temperature to 40 °C, at which temperature the reaction was continued for a total of 10 h. The stirring of the reaction mixture was promoted by turning on the homogenizer at approx. two hours after the beginning of the reaction. On the following day, the formic acid was evaporated out from the product under vacuum in the
15 course of approx. 5 h. At the same time the temperature of the product was gradually raised to 95 °C. After the distillation of the formic acid ended, the product was cooled and was packed in transport containers.

Samples of the reaction mixture were taken at 5 h, 8 h and 10 h. The formic acid was evaporated out from the samples by using a Rotavapor evaporator in a manner
20 corresponding to that described above. The electrical conductivity values of the products were measured as surface resistance measurements after processing according to Example 1. The resistances of the conductive polyaniline complex were $5.9 \times 10^5 \Omega/\text{sq}$ (5 h) and $5.66 \times 10^5 \Omega/\text{sq}$ (8 h) and that of the final product was $1.4 \times 10^5 \Omega/\text{sq}$. The best measurement result was achieved with the longest reaction time.

25 Example 3

Pilot-scale preparation of a composition with Ufacid K as the dodecylbenzenesulfonic acid

1.81 kg of polyaniline (Panipol Oy, EBR1 Lot 28) and 28.96 kg of dioctylphthalate plasticizer (Bisoflex DOP) were mixed in a reactor for 15 min. A doping acid mixture prepared by mixing 5.46 kg of dodecylbenzenesulfonic acid (Ufacid K) and 2.35 kg of an

85 % formic acid for 15 min at room temperature was added to the mixture. The acids were added in the course of approx. 20 min. During the adding, the temperature of the reaction mixture rose from room temperature to approx. 35 °C, at which temperature the reaction was continued for a total of 10 h. On the following day the formic acid was evaporated out from the product under vacuum in the course of approx. 5 h. At the same time the temperature of the product was gradually raised to 90 °C. After the distillation of the formic acid ended, the product was cooled and was used for preparing a conductive PVC film according to the following formula:

- 30 kg of the above-mentioned conductive polyaniline complex
- 10 ▪ 30 kg of emulsion PVC
- 1.2 kg of stabilizer
- 1.8 kg of carbon-black paste or titanium dioxide TiO₂ (colorant)

The materials were mixed together carefully. After the mixing, the mixture was comminuted further in a 3-roll mill in which the gap between the rollers had been adjusted to 40...50 µm. The roll-mill treatment rendered the mixture more homogeneous and minimized its granularity.

Thereafter, 12 kg of isopropanol was added to the comminuted mixture under careful mixing. After the mixing, a woven fabric was coated by the spread-coating or rotogravure method. The PVC film formed in connection with the coating was heated to approx. 165 °C, whereby it gelled to a completed product. Thereafter the film was turned over, and the other side was coated in the same manner. In the tests conducted, the surface resistance of the completed PVC film was 1.6E+05Ω/sq.

Example 4

Pilot-scale preparation of a composition with Ufacid TPB as the dodecylbenzenesulfonic acid

1.81 kg of polyaniline (Panipol Oy, EBR1 Lot 28) and 28.96 kg of dioctylphthalate plasticizer (Bisoflex DOP) were mixed in a reactor for 15 min. A doping acid mixture prepared by mixing 5.46 kg of dodecylbenzenesulfonic acid (Ufacid TPB) and 2.35 kg of an 85 % formic acid for 15 min at room temperature was added to the mixture. The acids

were added in the course of approx. 20 min. During the adding, the temperature of the reaction mixture rose from room temperature to approx. 35 °C, at which temperature the reaction was continued for a total of 10 h. On the following day, the formic acid was evaporated out from the product under vacuum in the course of approx. 5 h. At the same time, the temperature of the product was gradually raised to 90 °C. After the distillation of formic acid ended, the product was cooled. The product was cooled and was packed in transport containers for further treatment. The electrical conductivity property of a sample taken from the conductive polyaniline complex was measured. The resistance value obtained was 1.76E+07 Ω/sq. After the further process described in Example 3, the conductivity level was lower than in Example 3.

Because of the low electrical conductivity level, the reaction was continued, and 1.8 kg of formic acid was added to the product. The reaction time was 8 h. The formic acid was distilled off under vacuum in a manner corresponding to that above. The product was cooled and was packed in transport containers. The resistance value obtained for the product was 9.73E+05 Ω/sq.

The type of dodecylbenzenesulfonic acid has a significant effect on the preparation time of the composition, but the continuing of the reaction enhances the conductivity value significantly.

Example 5

Effects of mixing and the type of polyaniline on the quality of the end product

Three batches (5a, 5b and 5c) of composition were prepared using the formula of Example 3. In the first two experiments (5a and b) the polyaniline used was polyaniline EBR1 Lot 28, and in the subsequent experiment (5c) it was EBR Lot 29. The reaction was carried out as described in Example 3, except that in Experiment 5a a homogenizer was used for promoting mixing throughout the reaction at 1500 rpm and in Experiment 5b at 3000 rpm. In Experiment 5c the processing was carried out as in Experiment 5b. The conductivity levels of the products were measured as resistance measurements, as described in Example 1. The resistance values of the experiment products were 5a: 6.02E+04 Ω/sq, 5b: 2.35E+04 and 5c: 1.86E+06, estimated in the manner according to Example 3. It can be concluded

from the results that accelerating the stirring slightly lowered the resistance level. It was observed that the type of polyaniline also had an effect on the conductivity level of the end product.

Example 6

5 Effects of the processing temperature and the pre-mixing time

1.81 kg of polyaniline (Panipol Oy, EBR1 Lot 29 and 28.96 kg of dioctylphthalate plasticizer (Bisoflex DOP) were mixed in a reactor for 60 min. The mixing was enhanced using a homogenizer (3000 rpm). During the mixing, the temperature of the reaction mixture was raised to 45 °C. A doping acid mixture prepared by mixing 5.46 kg of
10 dodecylbenzenesulfonic acid (Ufacid K) and 2.35 kg of an 85 % formic acid for 15 min at room temperature was added to the mixture. The acids were added in the course of 10 min. During the adding the rotation speed of the homogenizer was lowered to 1500 rpm and was doubled after the adding. After the adding, the temperature of the reaction mixture was raised to 50 °C, at which temperature the reaction was continued for a total of 10 h. On the
15 following day, the formic acid was distilled out from the product under vacuum in the course of approx. 5 h. At the same time, the temperature of the product was gradually raised to 95 °C. After the distillation of the formic acid ended, the product was cooled and was packed in transport containers.

A conductive PVC film was prepared in the manner described in Example 3, without a
20 roll-mill treatment. The conductivity level of the end product was determined as a surface resistance measurement, and it was $1.25\text{E}+04 \text{ } \Omega/\text{sq}$. The result indicates that the quality of the conductive complex was clearly better, since roll-mill treatment is not necessary. At the same time the result indicates the favorable effect of the raising of the processing temperature and the pre-mixing time on the quality of the product.

25 **Example 7A**

Dodecylbenzenesulfonic acid Ufacid TPB

4.68 g of polyaniline (Panipol Oy, EBR1 Lot 28) and 80.2 g of C₇-C₉ dialkylphthalate plasticizer (Bisoflex L79P) were mixed with a magnetic stirrer in a reactor for 5 min. A doping acid mixture prepared by mixing 15.12 g of dodecylbenzenesulfonic acid (Ufacid

TPB) and 6.5 g of an 85 % formic acid for 5 min at room temperature was added to the mixture. The acids were added in the course of approx. 10 min. During the adding, the temperature of the reaction mixture rose from room temperature to approx. 35 °C, at which temperature the reaction was continued for a total of 24 h by stirring the mixture throughout the reaction with a magnetic stirrer. On the following day, the formic acid was distilled out from the product under vacuum in the course of approx. 8 h. At the same time the temperature of the product was gradually raised to 55 °C. After the distillation of the formic acid ended, the product was cooled. A conductive PVC film was prepared on a laboratory scale according to the following formula:

- 10 ▪ 50 g of the above-mentioned conductive polyaniline complex
- 50 g of emulsion PVC
- 2 g of stabilizer
- 3 g of carbon-black paste or titanium dioxide TiO₂ (colorant)

The materials were mixed together carefully. After the mixing, the mixture was comminuted further in a paste mill. The paste-mill treatment rendered the mixture more homogeneous and minimized its granularity.

Thereafter 20 g of isopropanol was added to the comminuted mixture under careful mixing. After the mixing, a woven textile fabric was coated on both sides by the spread-coating method. The PVC film formed in connection with the coating was kiln-treated at 165 °C for 2.5 minutes, whereby it gelled to form a completed product. In the tests conducted, the surface resistance was 1.0+E5 Ω/sq.

Example 7B

Ufacid K as the dodecylbenzenesulfonic acid

An experiment according to Example 7A was performed by merely replacing the dodecylbenzenesulfonic acid type Ufacid TPB with Ufacid K. The conductive complex had a lower viscosity and was easier to process than the complex according to Example X A. In the tests conducted, the surface resistance of the end product was 1.5+E5 Ω/sq.

Example 7C

Ufacid KW as the dodecylbenzenesulfonic acid

5 An experiment according to Example 7A was performed by merely replacing the dodecylbenzenesulfonic acid type Ufacid TPB with Ufacid KW. The conductive complex had a lower viscosity and was easier to process than the complex according to Example 7A. In the tests conducted the surface resistance of the end product was inferior to that in Examples 7A and 7B, being approx. $2.0 \times 10^6 \Omega/\text{sq}$.

Claims:

1. An electrically conductive plasticizer composition having an electrical conductivity of $10^{-2} \dots 10^{-9}$ S/cm, **characterized** in that it comprises 50 – 95 parts by weight of a plasticizer for thermoplastics and 50 – 5 parts by weight of polyaniline and its counter-ion,
5 which together form a doped polyaniline complex dissolved or dispersed in the plasticizer.
2. The plasticizer composition according to Claim 1, **characterized** in that the plasticizer for thermoplastics is a dialkyl phthalate; a dialkyl terephthalate; a trialkyl or triaryl phosphate; an aliphatic acid ester, such as dialkyldiapatate or dialkylsebasate; a sulfonic or benzenic acid ester; an epoxidized oil, or a mixture thereof.
- 10 3. The plasticizer composition according to Claim 1 or 2, **characterized** in that the plasticizer is a dialkyl phthalate the alkyl groups of which are the same or different and comprise a linear or branched carbon chain of 1 – 9 carbon atoms.
4. The plasticizer according to Claim 3, **characterized** in that the plasticizer is dioctyl phthalate or di-iso-octyl phthalate.
- 15 5. The plasticizer composition according to any of the preceding claims, **characterized** in that the counter-ion for the polyaniline is derived from dodecylbenzenesulfonic acid, camphor sulfonic acid, p-toluenesulfonic acid or phenolsulfonic acid, or a mixture of thereof.
6. The plasticizer composition according to any of the preceding claims, **characterized**
20 in that, mixed with a PVC emulsion, the composition forms a substantially non-migrating PVC blend.
7. The plasticizer composition according to any of the preceding claims, **characterized** in that it comprises approx. 3 – 8 parts by weight of polyaniline, approx. 70 – 90 parts by weight of plasticizer, and approx. 5 – 20 parts by weight of a counter-ion for the
25 polyaniline, the amount of the counter-ion being in parts by weight approx. 2- to 4-fold that of the amount of polyaniline.

8. The plasticizer composition according to any of Claims 1 – 5, **characterized** in that it contains an inorganic compound, such as zinc oxide, which neutralizes the excess of the dopant.
9. A process for the preparation of an electrically conductive plasticizer composition,
5 **characterized** in that
- a plasticizer is mixed with a polyaniline in a non-conductive form in order to form a plasticizer mixture, and
 - a counter-ion for the non-conductive polyaniline is added to the plasticizer mixture to dope the polyaniline and to form a doped plasticizer composition.
- 10 10. The process according to Claim 9, **characterized** in that to the plasticizer mixture a dopant mixture is added which comprises a counter-ion for the polyaniline and an activator capable of accelerating the doping.
11. The process according to Claim 10, **characterized** in that the activator is a volatile compound, which is removed from the plasticizer composition by evaporation.
- 15 12. The process according to Claim 10 or 11, **characterized** in that the activator is formic acid or acetic acid.
13. The process according to any of Claims 9 – 12, **characterized** in that 3 – 8 parts by weight of polyaniline and approx. 70 – 90 parts by weight of plasticizer are mixed together to form a plasticizer mixture, and to this mixture a dopant mixture is added, containing
20 approx. 5 – 20 parts by weight of a counter-ion for the polyaniline and 1 – 10 parts by weight of activator.
14. The process according to any of Claims 9 – 13, **characterized** in that the ingredients of the plasticizer composition are mixed together substantially without additional heating.
15. The process according to any of Claims 9 – 14, **characterized** in that the doped
25 plasticizer composition is mixed for 1 – 48 hours at approx. 30 – 50 °C.

16. The process according to any of Claims 10 – 15, **characterized** in that the activator is removed by means of vacuum and by raising the temperature of the composition to approx. 35 – 150 °C
17. The process according to any of Claims 10 – 16, **characterized** in that the polyaniline is EB (emeraldine base), the plasticizer for thermoplastics is a dialkyl phthalate; a dialkyl terephthalate; a trialkyl or triaryl phosphate; an aliphatic acid ester, such as dialkyldiapatate or dialkyl sebasate; a sulfonic or benzenic acid ester; an epoxidized oil; or a mixture thereof, and the polyaniline dopant used is dodecylbenzenesulfonic acid, camphor sulfonic acid, p-toluenesulfonic acid or phenolsulfonic acid, or a mixture thereof.
18. A process for the preparation of an electrically conductive PVC film, **characterized** in that
- 10 – 50 parts by weight of the plasticizer composition according to Claim 1, 1 – 90 parts by weight of a PVC emulsion, and 0 – 10 parts by weight of auxiliary agents and colorants, known *per se*, are mixed to form a PVC mixture,
 - the mixture is spread on a substrate to form a continuous layer, and
 - the layer is allowed to solidify to form a film.
19. The process according to Claim 18, **characterized** in that the layer is solidified by bringing it to a temperature of at least 120 °C, preferably at least 150 °C.
20. The process according to Claim 18 or 19, **characterized** in that the PVC mixture is comminuted and possibly diluted before being spread onto the substrate.
21. The process according to any of Claims 18 – 20, **characterized** in that the plasticizer composition, the PVC emulsion, and any auxiliary agents and colorants are mixed together in a dissolver or a roll mill or a corresponding mixing apparatus.
22. The process according to any of Claims 18 – 21, **characterized** in that to the PVC mixture there is further added a plasticizer for PVC, the plasticizer being a dialkyl phthalate; a dialkyl terephthalate; a trialkyl or triaryl phosphate; an aliphatic acid ester, such as dialkyl diapatate or dialkyl sebasate; a sulfonic or benzene acid ester; an epoxidized oil, or a mixture thereof.

23. The process according to any of Claims 18 – 22, **characterized** in that the substrate comprises a woven textile fabric or a paper substrate.

24. The process according to any of Claims 18 – 23, **characterized** in that the surface resistance of the product coated with the PVC film is at least approx. $1 * 10^6 \Omega/\text{sq.}$

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 02/00053

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: H01B 1/12, H01B 1/20, C08K 5/00, C08L 79/02, C08L 27/06
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C08K, C08L, H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI-DATA, CHEM.ABS-DATA, DIALOG FILE 34:SCISEARCH

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| X | EP 0643397 A1 (NESTE OY), 15 March 1995 (15.03.95), page 4, line 37 - line 46; page 6, line 4 - line 13; page 6, line 57 - page 7, line 21 -- | 1,5-7 |
| X | EP 0797218 A2 (INTERNATIONAL BUSINESS MACHINES CORP), 24 Sept 1997 (24.09.97), page 3, line 7 - line 20; page 3, line 50 - line 53, abstract -- | 1-2 |
| X | WO 9919391 A1 (ZIPPERLING KESSLER & CO), 22 April 1999 (22.04.99), claims 1-4, abstract -- | 1 |

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| A | EP 0721194 A2 (INTERNATIONAL BUSINESS MACHINES CORP), 10 July 1996 (10.07.96), page 2, line 30 - line 48; page 6, line 1 - line 5, abstract -- | 1-24 |
| A | WO 9805040 A1 (COMMISSARIAT A L'ENERGIE ATOMIQUE), 5 February 1998 (05.02.98), abstract -- | 1-24 |
| A | Journal of Applied Polymer Science, Vol 69, 1998, A L G Saad et al: "Studies of Electrical and Mechanical Properties of Semiconductive Poly (vinyl chloride) Compositions", p 685-693 -- | 1-24 |
| A | Journal of Polymer Science: Part A Polymer Chemistry, Vol 33, 1995, Jadwiga Laska et al: "Phosphoric Acid Diesters Protonated Polyaniline: Preparation, Spectroscopic Properties, and Processability", p 1437-1445 -- | 1-24 |
| A | Journal of Applied Polymer Science, Vol 61, 1996 Jadwiga Laska et al: "Rheological Behavior of Plasticized Polyaniline", p 1339-1343 -- | 1-17 |
| A | Synthetic Metals, Vol 84, 1997, Jadwiga Laska et al: "Conducting blends of polyaniline with conventional polymers", p 117-118 -- | 1-24 |
| A | Synthetic Metals, Vol 84, 1997, J Tanner et al: "Conductivity tailoring of blends of fusible polyaniline and polyolefins by viscosity ratio" p 763-764 -- | 1-24 |

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 02/00053

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|---|---|-----------------------|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| P,A | Journal of Applied Polymer Science, Vol 82, 2001, Roselena Faez et al: "Elastic Polyaniline with EPDM and Dodecylbenzenesulfonic Acid as Plasticizers", p 1768-1775 -- | 1-24 |
| P,A | Journal of Applied Polymer Science, Vol 80, 2001, Raji K Paul et al: "Melt/Solution Processable Polyaniline with Functionalized Phosphate Ester Dopants and Its Thermoplastic Blends", p 1354-1367 -- | 1-24 |
| A | WO 9941756 A1 (ZIPPERLING KESSLER & CO), 19 August 1999 (19.08.99), abstract -- | 1-24 |
| A | EP 0497514 A1 (AMERICHEM INC), 5 August 1992 (05.08.92), abstract -- | 1-24 |
| A | US 5595689 A (KULKARNI ET AL), 21 January 1997 (21.01.97), abstract -- | 1-24 |
| A | FI 101075 B (NESTE OY), 15 April 1998 (15.04.98), abstract -- ----- | 18-24 |

Form PCT/ISA/210 (continuation of second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT
Information on patent family members

01/05/02

Internauonal application No.

PCT/FI 02/00053

| Patent document cited in search report | | | Publication date | Patent family member(s) | | Publication date |
|---|---------|----|---------------------|----------------------------|--------------|---------------------|
| EP | 0643397 | A1 | 15/03/95 | CN | 1046750 B | 24/11/99 |
| | | | | CN | 1130390 A | 04/09/96 |
| | | | | DE | 69422108 D,T | 31/05/00 |
| | | | | JP | 7126384 A | 16/05/95 |
| | | | | US | 5783111 A | 21/07/98 |
| | | | | WO | 9506685 A | 09/03/95 |
| EP | 0797218 | A2 | 24/09/97 | JP | 10046027 A | 17/02/98 |
| | | | | KR | 217533 B | 01/09/99 |
| | | | | TW | 434273 B | 00/00/00 |
| | | | | US | 5932143 A | 03/08/99 |
| | | | | US | 6210606 B | 03/04/01 |
| | | | | US | 5969024 A | 19/10/99 |
| | | | | JP | 3158059 B | 23/04/01 |
| | | | | JP | 9279040 A | 28/10/97 |
| | | | | KR | 221515 B | 01/10/99 |
| | | | | US | 5928566 A | 27/07/99 |
| WO | 9919391 | A1 | 22/04/99 | US | 5871671 A | 16/02/99 |
| EP | 0721194 | A2 | 10/07/96 | JP | 3103030 B | 23/10/00 |
| | | | | JP | 8231863 A | 10/09/96 |
| | | | | KR | 225392 B | 15/10/99 |
| | | | | US | 5804100 A | 08/09/98 |
| | | | | US | 5962632 A | 05/10/99 |
| | | | | US | 6312620 B | 06/11/01 |
| | | | | JP | 3065524 B | 17/07/00 |
| | | | | JP | 8231862 A | 10/09/96 |
| | | | | KR | 209043 B | 15/07/99 |
| | | | | US | 5736623 A | 07/04/98 |
| | | | | US | 6087472 A | 11/07/00 |
| WO | 9805040 | A1 | 05/02/98 | EP | 0916141 A | 19/05/99 |
| | | | | FR | 2751660 A,B | 30/01/98 |
| | | | | JP | 2001501017 T | 23/01/01 |
| | | | | US | 6235220 B | 22/05/01 |
| WO | 9941756 | A1 | 19/08/99 | US | 5908898 A | 01/06/99 |
| EP | 0497514 | A1 | 05/08/92 | AT | 150577 T | 15/04/97 |
| | | | | CA | 2059945 A | 01/08/92 |
| | | | | DE | 69218274 D,T | 28/08/97 |
| | | | | JP | 4318069 A | 09/11/92 |
| | | | | US | 5217649 A | 08/06/93 |
| US | 5595689 | A | 21/01/97 | NONE | | |
| FI | 101075 | B | 15/04/98 | FI | 935889 A | 29/06/95 |

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(54) Title: ELECTRICALLY CONDUCTING PLASTICIZER COMPOSITION AND PROCESS FOR THE PRODUCTION THEREOF

(57) Abstract: The invention relates to an electrically conductive plasticizer composition and to a process for the preparation thereof. The composition according to the invention comprises 50-95 parts by weight of a plasticizer for thermoplastics and 50-5 parts by weight of polyaniline and its counter-ion, which together form a doped polyaniline complex dissolved or dispersed in the plasticizer. By means of the invention it is possible to prepare, for example, an electrically conductive PVC film by mixing together 10-50 parts by weight of the plasticizer composition, 1-90 parts by weight of a PVC emulsion and 0-10 parts by weight of auxiliary agents and colorants, known *per se*, to form a PVC mixture, by spreading the mixture onto a substrate to form a continuous layer, and by solidifying the composition to form an electrically conductive film.



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